Selective Saturation and Inversion of Multiple Resonances in High Resolution Solid State ^{13}C CP/MAS Experiments

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Abstract

Taking advantage of the long ^{13}C T_1 values generally encountered in solids, selective saturation and inversion of more than one resonance in ^{13}C CP/MAS experiments can be achieved by sequentially applying several DANTE pulse sequences centered at different transmitter frequency offsets. A new selective saturation pulse sequence is introduced composed of a series of 90° DANTE sequences separated by interrupted decoupling periods during which the selected resonance is destroyed. Applications of this method, including the simplification of the measurement of the principal values of the ^{13}C chemical shift tensor under slow MAS conditions are described. The determination of the aromaticity of coal using a relatively slow MAS spinning rate is also described.

Keywords: DANTE, multiple offset DANTE, coal structure, ^{13}C NMR

INTRODUCTION

It is well known that high resolution isotropic chemical shift spectra in solids can be obtained by applying high power heteronuclear decoupling in combination with MAS at a spinning rate larger than the width of the chemical shift anisotropy (CSA). Although isotropic chemical shifts are very useful in determining chemical structure, they come at a high price as the sample spinning averages the tensorial parameters which provide a great deal of information about the local electronic environment of the nuclei and molecular dynamics. However, when the sample spinning rate is less than the width of the chemical shift anisotropy (i.e., the slow MAS condition), the CSA powder pattern collapses to a group of spinning sidebands (SSB) spaced at the sample rotation rate with the center band located at the isotropic chemical shift position. As was demonstrated by Herzfeld and Berger (1), the tensorial principal values can be retrieved through digital simulation of the intensities of just a few spinning sidebands. However, when there are several chemically unequivalent nuclei in a molecule, the spinning sideband patterns are superimposed in the classical one dimensional CP/MAS experiment and it becomes very difficult to separate the individual sideband patterns and measure accurate intensities due to overlapping of lines. In order to simplify this measurement, a few two dimensional MAS experiments have been developed in which the isotropic chemical shift is obtained in one dimension while the spinning sideband patterns for each spin are separated in the second dimension (2,3). However, these methods suffer from either the need for specialized equipment and relaxation difficulties in the case of the switched speed method (2) or from intensity distortion problems in the case of the TOSS-Reversed TOSS method (3). It will be shown in this paper that undistorted spinning sideband patterns for only the aliphatic carbons can be readily obtained by saturating the entire aromatic, carbonyl and carboxyl sideband families using several DANTE sequences at different transmitter offset frequencies.

There are basically three categories of selective pulses; 1) the soft pulse (4-6) which is a single long, weak rectangular pulse; 2) the shaped pulse (7,8); and 3) the DANTE pulse sequence which consists of a series of short intense rf pulses (9-11). It has been known for a decade that selective excitation experiments in liquid state high resolution spectroscopy are quite informative (12). In solid state experiments, attention has initially been focused on selective excitation of multiple quantum coherence in quadrupolar systems (13-17) and on the application of selective excitation to either a static or high speed MAS sample. In both cases no spinning sidebands need be considered (18). In 1983, Caravatty et al. (19) demonstrated the usefulness of selective irradiation under slow MAS conditions and concluded that uniform excitation of one spinning sideband family can be achieved by synchronizing the pulse train of the DANTE sequence with sample rotation. It is possible to saturate the longitudinal magnetization of an entire sideband family by selective irradiation of one of its sidebands, while it is not possible to excite the whole sideband family via selective sideband irradiation. An example of this important feature is provided by Tekely et al. (20), where an incomplete elimination of the broad aromatic band and its spinning sidebands in a ^{13}C CP/MAS spectrum of coal at high magnetic field was achieved by applying a long DANTE sequence. Recently, Tekely et al (21) have reported a new selective pulse sequence named SELDOM; this sequence employs the normal 90° hard pulse and takes advantage of the short T_2 values generally encountered with solids. This pulse sequence preserves the magnetization of the preferred spin along the z axis while destroying all components of magnetization corresponding to the other spins presented in the spectrum. Selective pulses have also been successfully applied to simplify ^{13}C CSA measurement in 1D MAS-OFFMAS switched-angle experiments (22-23).

However, selective experiments to date have mainly focused on the selective excitation or saturation of one particular resonance or chemical shift range in the spectrum. If more than one resonance or chemical shift range could be inverted or saturated before the detection period, these experiments would have a broad range of applications. Some efforts have been made in the past to selectively excite more than one resonance. In the Double-DANTE sequence (11), selective excitation at two arbitrary frequencies can be achieved by the modulation of the phase of the DANTE sequence. Another demonstration provided by Ashida et al (23) in their 1D switched angle experiment showed that the inversion of two signals can be realized by sequentially applying two long soft pulses at different frequencies.

It will be demonstrated in this paper that selective saturation or inversion of multiple resonances can be achieved in spin systems with long spin lattice relaxation times by sequentially applying multiple DANTE sequences at different transmitter frequency offsets. In addition, a variation of the basic DANTE sequence which efficiently saturates the selected resonance is introduced. Several applications will be presented of this multiple resonance selective method which we will denote as "multiple offset DANTE". Experiments presented include spectra of complex organic compounds containing only one or two sideband families by saturation of the remaining resonances. This allows for more accurate determination of the sideband intensities and resultant principal components of the chemical shift tensor through removal of overlapping lines. The carbon aromaticity of coals can also be determined by the saturation of the entire aromatic region. Finally, with the addition of standard dipolar dephasing techniques to the multiple offset DANTE method, a spectrum containing only the spinning sideband family of a single aromatic carbon type (i.e., protonated, substituted, condensed, or phenolic) of a low rank coal can be obtained.

EXPERIMENTAL

All of the ^{13}C CP/MAS and selective irradiation experiments were performed on a Varian VXR-200 NMR spectrometer with a ^{13}C frequency of 50.318 MHz, using a CP/MAS probe from Doty Scientific Inc. A 50 KHz rf field strength was applied during the cross polarization period for both the ^{13}C and ^{1}H spin systems. When either higher decoupling rf field or higher selectivity for the DANTE sequence was necessary, the transmitter power levels of both channels were switched to the required level separately.

The basic pulse sequence used to perform the multiple offset DANTE is shown in Figure 1a. It starts with a classical cross polarization procedure to enhance the sensitivity of the observed rare nuclei (^{13}C), followed by a nonselective $90°_y$ pulse used to rotate the prepared magnetization back along the z axis. This is then followed by a series of DANTE sequences in which the transmitter frequency offset is changed. For the ith DANTE sequence, the parameters are as follows: transmitter frequency offset to$_i$, pulse width T_{pi}, pulses interval T_{di}, and number of pulses N_i. Each DANTE sequence is, as shown in Figure 1b, a series of small tip angle pulses. If the cumulative total of the small tip angles is 180°, the net effect is inversion of the selected resonance whereas the selected resonance is saturated or destroyed by a long pulse train. An interrupted decoupling period DD$_i$ is inserted between the DANTE sequences to allow the residual transverse magnetization to be fully destroyed before the next DANTE sequence starts; this delay time also serves for the switching time of the transmitter frequency offset. At the end of the DANTE group, a nonselective 90° pulse is used to return the magnetization to the x-y plane. Data acquisition then starts under the condition of high power proton decoupling.

In order to understand how these sequences work, several important features of the DANTE sequence must be reviewed. The selectivity of irradiation, v_i, is approximately determined by the average rf strength $v_i=\gamma H_1[T_{pi}/(T_{pi}+T_{di})]$, where γH_1 is the pulse field strength in Hz. The magnetization corresponding to those non-selected spins is nearly unperturbed at the end of each individual DANTE sequence, i.e., after the first DANTE sequence they remain at their original longitudinal position. The second DANTE sequence acts in an identical manner, preparing the magnetization situated at to2 from its longitudinal position to its predesignated state, while the other resonances outside the selectively irradiated range, including the resonance at to$_1$, remain unperturbed. The first irradiated resonance still remains in its prepared state as long as its T1 is relatively long compared to the length of the DANTE sequence. In the same manner, additional resonances can be prepared by the application of more DANTE sequences at different transmitter offsets.

A variation of the DANTE sequence which has been found to be very powerful in performing saturation in solids is shown in Figure 1c. In this variation the classical long DANTE sequence, shown in Figure 1b, is replaced by a group of sub-DANTE sequences with the cumulative flip angle for each sub-DANTE sequence set to 90°. A dipolar dephasing period inserted between each of the sub-DANTE sequences destroys the transverse magnetization selectively produced by each sub-DANTE sequence. The dephasing time needed depends on the strength of the C-H dipolar coupling; however, a longer time can be used since the magnetization of the spins of interest remains along the z axis during these dephasing periods. This variation of the normal DANTE sequence is called the "dephased DANTE" sequence in the following discussion. It functions in a manner opposite to the SELDOM pulse sequence (21), by destroying only the longitudinal magnetization corresponding to the resonance line selected while leaving the remaining resonances unperturbed.

Hexamethylbenzene (HMB) and 1,2,3-trimethoxybenzene (TMB) were obtained from Aldrich and used as received. The Lewiston Stockton coal sample is from the Argonne Premium Coal Sample Bank. Simulation of the intensity pattern of a spinning sideband family was performed using a program similar to that described in the literature by Fenzke et al (24).

RESULTS AND DISCUSSIONS

The efficiency of the dephased DANTE sequence, demonstrated on HMB, is shown in Figure 2. In this test case the resonance for the methyl carbons in HMB is saturated by using both the classical long DANTE pulse train (Figure 2b) and the dephased DANTE sequence (Figure 2c). It is obvious that the longitudinal magnetization of the methyl carbons is still appreciable after the application of 400 pulses using the classical DANTE sequence, whereas 60 pulses are sufficient to destroy the magnetization with the use of the dephased DANTE sequence. The dephased DANTE sequence can be used to replace the individual DANTE sequence in Figure 1a to perform signal saturation. It should be noted that the efficiency of the dephased DANTE sequence decreases as the number of spinning sideband of the saturated resonance increases unless synchronized sample rotation is used.

A typical example of the multiple offset DANTE method is given in Figure 3. Figure 3a is the ^{13}C CP/MAS spectrum of TMB under fast spinning conditions. There are four peaks in the aromatic region with isotropic chemical shifts of 105, 124, 138 and 154 ppm. Figure 3b shows the resultant spectrum obtained by inverting the two outer peaks using the classical 180°-DANTE at to_1=105 and to_2=154 ppm and saturating the two inner peaks using the dephased DANTE sequence at to_3=124 and to_4=138 ppm. It is clear that the multiple offset DANTE pulse sequence works.

The application of this pulse sequence in cases of slow MAS spinning in order to retrieve the shielding tensor components is shown in Figure 4. Figure 4a is the classical ^{13}C CP/MAS SSB spectrum of TMB obtained at a spinning rate of 1106 Hz. This spectrum is very crowded and the sidebands from the aromatic carbons and aliphatic carbons overlap as expected. By using three DANTE sequences at different transmitter frequency offsets, one is left with the spinning sideband spectrum containing only the three methyl carbons and the C2 aromatic carbon (138 ppm), as shown in Figure 4b. The frequency offset is chosen such that the selectively irradiated frequency is on one of the spinning sidebands with relatively high intensity in the selected sideband family. In addition, this irradiated sideband should not be superimposed with the sidebands from any of the carbons whose magnetization is to be preserved. Figure 4c contains only the sideband patterns from the methyl carbons and was obtained by saturation of all of the aromatic carbon resonances using four DANTE sequences. In order to avoid perturbation of the methyl groups, the transmitter frequency offsets were set to the downfield first sideband positions instead of the central isotropic peaks for the two protonated carbons (105 and 124 ppm). The chemical shift tensor principal values for the three methyl carbons, obtained by simulation of the intensity distribution patterns, along with the values obtained from a single crystal study (25) are listed in Table 1. The two sets of data are consistent within experimental error. It should also be noted that the SSB pattern for the unsaturated C2 aromatic carbon in Figure 4b looks very similar to that in the classical CP/MAS spectrum (Figure 4a), demonstrating the selectivity of the pulse sequence. The intensity of the lines in Figure 4b for the non-saturated C2 are not perturbed even though there are sidebands of this carbon within 300 Hz of the saturating frequency. The principal values for C2 obtained for both experiments are within the experimental error for this technique, and these values are also close to the single crystal results (see Table 1). Similar

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experiments were performed to isolate the sideband pattern of the other aromatic carbons, with the resulting tensor components also reported in Table 1. Thus, this multiple offset DANTE method can be used to perform tailored excitation to obtain the tensor components of carbons in complex solids where either a single crystal or 2D experiments were previously required.

The application of the multiple offset DANTE sequence to an even more complex sample is demonstrated in Figure 5 for a Lewiston-Stockton coal sample. This coal has been well characterized by NMR measurements in our laboratory (26) as well as by other researchers (27). In this case, the experiments are performed under conditions of moderate (2-4 KHz) spinning rates in order not to attenuate the cross polarization magnetization transfer mechanism for carbons with weak dipolar interactions (28). However, at this spinning rate the sidebands produced by the aromatic carbons will be superimposed on the aliphatic signal as is shown in Figure 5a. A second spectrum, Figure 5b is obtained by total elimination of the aromatic spinning sideband family using four DANTE sequences with transmitter frequency offsets of 110, 126, 138, 150 ppm (26). It is clear from this figure that the elimination of the aromatic signal is complete. Figure 5c is the difference between Figures 5a and 5b, and shows only the signal from the aromatic carbons. From the integrated signal intensities of these spectra a carbon aromaticity of 0.77 is calculated, in good agreement with the value of 0.75 obtained from a Bloch decay measurement performed at 100 MHz with a spinning rate of 4 KHz (29). This agreement again lends confidence in the high degree of selectivity of this method.

This type of tailored excitation is even more efficient for extracting the ^{13}C CSA information from a complex compound such as a low rank coal under slow MAS condition when combined with the dipolar dephasing technique. In this case, a rotational synchronized dipolar dephasing sequence (30) is incorporated into the pulse sequence in Figure 1a to suppress the signal from protonated carbons. The data in Figures 6a and 6b were obtained in the same fashion as in Figures 5a and 5b on the Lewiston Stockton coal but with the addition of a 50 μs dephasing period to suppress the signal from the protonated carbons. Only the sideband families from the nonprotonated aromatic carbons as well as the mobile methyl resonances remain in Figure 6a and only the mobile methyl carbons remain in Figure 6b. Figure 6c is obtained by inserting a 50 μs dipolar dephasing time followed by three DANTE sequences centered at 155, 145, and 138 ppm in order to achieve complete saturation of the rather large chemical shift range of the phenolic and substituted carbons. The resulting spectrum contains signals due to the condensed aromatic carbons (i.e., bridgehead), and the mobile methyl carbons. A 50 μs dephasing time is again inserted and followed by four DANTE sequences with transmitter frequencies at 150, 125, 120 and 110 ppm, respectively, in order to saturate the phenolic and inner aromatic carbons, leaving essentially only the signal from the substituted aromatic carbons along with that from the mobile methyl carbons (Figure 6d). By a linear combination of the spectra in Figures 5 and 6, it is possible to obtain the sideband patterns for the protonated, the condensed, as well as the substituted aromatic carbons. For example, the condensed aromatic sideband family is obtained by subtracting 6b from 6c, and the substituted aromatic sideband family can be isolated by subtracting 6b from 6d. The ^{13}C CSA tensor principal values obtained by digital simulation of these sideband patterns for each type of carbon are listed in Table 2. These values are similar to those reported in coals by using static powder pattern simulation and variable angle spinning experiments (31).

Now, let us consider the limitations of the multiple offset DANTE discussed above. First, the prepared magnetization before the last DANTE sequence will relax to its equilibrium state according to its individual spin-lattice relaxation time, T_1. It generally takes 5 to 20 ms to prepare each resonance, thus limiting the number of resonances that can

be prepared. Fortunately, ^{13}C T_1 values in solids are generally very long, ranging from seconds to tens of seconds. If different values of T_1 exist, the resonance with the longest T_1 should be selectively irradiated first while the resonance with the shortest T_1 should be selected last. A second limitation arises from using normal rectangular pulses in the DANTE sequence which cause excitation not only at the center frequency, but also at other frequencies determined by the pulse length and spacing applied (10). This leads to a slight intensity loss at these other frequencies,. or to a distortion in the baseline. Although this loss is small, it can become significant as the number of DANTE sequences increases. This loss could be reduced or eliminated with the use of a more selective pulse, such as shaped pulses (7-8).

CONCLUSIONS

Multiple resonance saturation and inversion in a solid state spin system with relatively long T_1 values can be easily achieved by using multiple DANTE pulse sequences at different transmitter frequency offsets. A powerful saturation pulse sequence (i.e., the dephased DANTE sequence) is proposed. This type of multiple resonance saturation method can be successfully applied to perform the spinning sideband separation in slow MAS experiments, including tailored excitation of a spinning sideband family of a single aromatic carbon type in a low rank coal. This method can also be applied to additional problems in solids, such as monitoring the spin diffusion process among carbons. In addition, the selective pulse sequence is not limited to the DANTE sequence; other sequences such as a soft pulse or a shaped pulse could be used in place of the DANTE sequence. This type of multiple resonance method based on changing the transmitter frequency offsets should also be useful in high resolution liquid state NMR, as long as the spin system under investigation has relatively long spin-lattice relaxation times.

ACKNOWLEDGMENT

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Table 1. Principal values of ^{13}C chemical-shift tensors obtained through digital simulation of sideband intensity patterns[a]

Assignment	σ_{11}	σ_{22}	σ_{33}	σ_{avg}
		1,2,3-trimethoxybenzene		
M_1	82(83)	72(71)	9(9)	54
M_2	87(88)	84(83)	10(10)	60
M_3	81(82)	71(70)	13(13)	55
$C_{1,3}$	221(218)	168(172)	72(73)	154
$C_2{}^b$	174(179)	169(164)	71(71)	138
$C_2{}^c$	172	171	71	138
$C_{4,6}$	190(187)	119(123)	10(7)	106
C_5	229(227)	133(136)	11(10)	124

[a]Data in parentheses are single crystal results (25).
[b]Obtained using sideband intensities from Figure 4a.
[c]Obtained using the sideband intensities in Figure 4b.

Table 2. Principal values of ^{13}C chemical shift tensors obtained through digital simulation of sideband intensity patterns for the Lewiston Stockton Coal

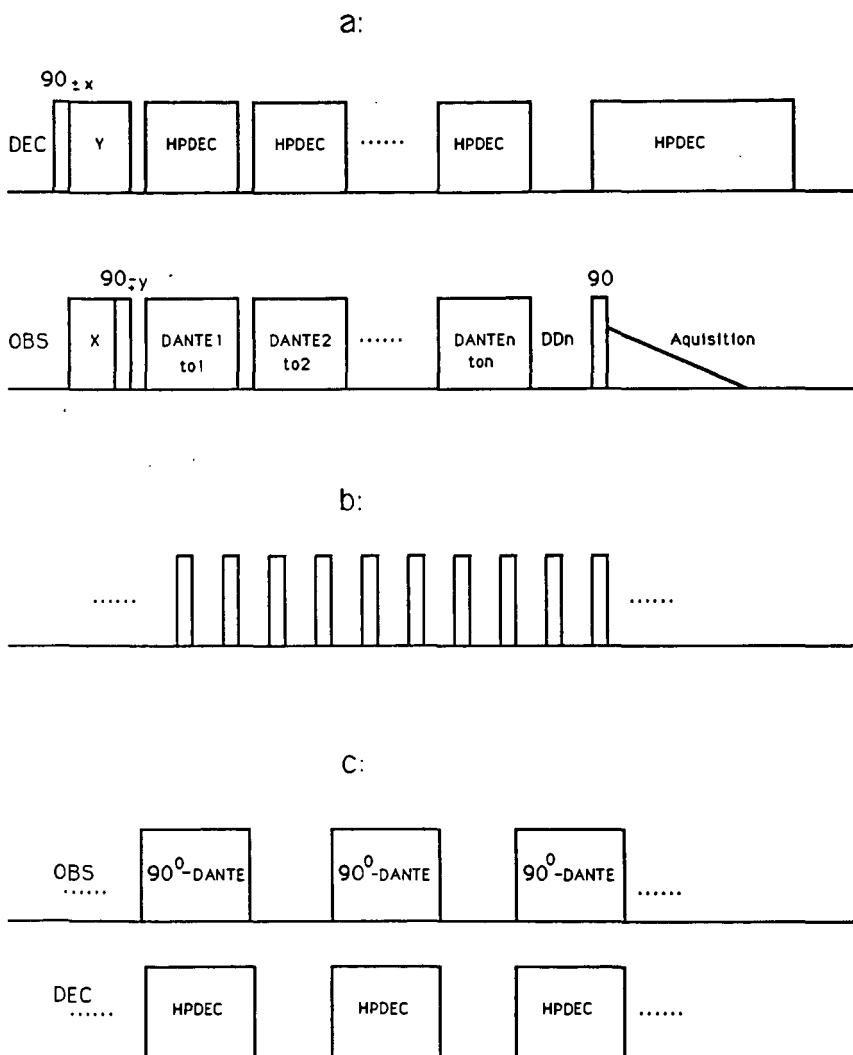| Assignment	σ_{11}	σ_{22}	σ_{33}	σ_{avg}
Protonated	230	126	14	123
condensed	192	184	2	126
substituted	238	158	18	138

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Figure 1. Pulse sequences: a) the general pulse sequence used to perform multiple resonance saturation and inversion, with the parameters for the ith DANTE sequence: transmitter frequency offset to_i, pulse width T_{pi}, pulse interval T_{di} and the number of pulses N_i; b) the classical DANTE sequence; c) the dephased DANTE sequence.
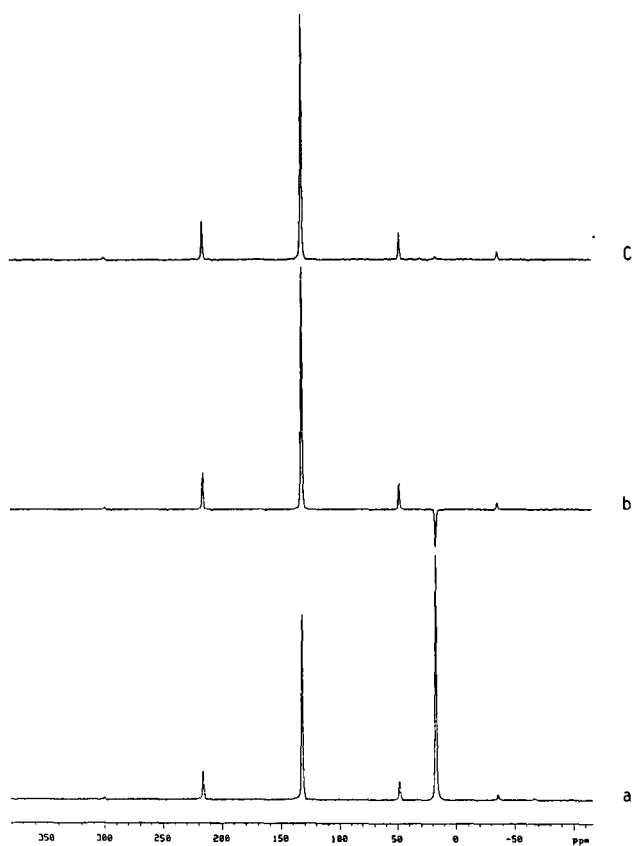
Figure 2. ^{13}C CP/MAS spectra of HMB obtained with sample spinning rate of 4.2 KHz, contact time of 3 ms, and 64 scans: a) the normal ^{13}C CP/MAS spectrum; b) saturation of the methyl carbon using the classical DANTE sequence with 400 hard pulses, pulse width 0.25 μs and the interval between pulses 50 μs; c) saturation of the methyl carbon using the dephased DANTE sequence with three sub-DANTE sequences, each containing 20 hard pulses with the same parameters as in b, and a dephasing time of 16 ms.
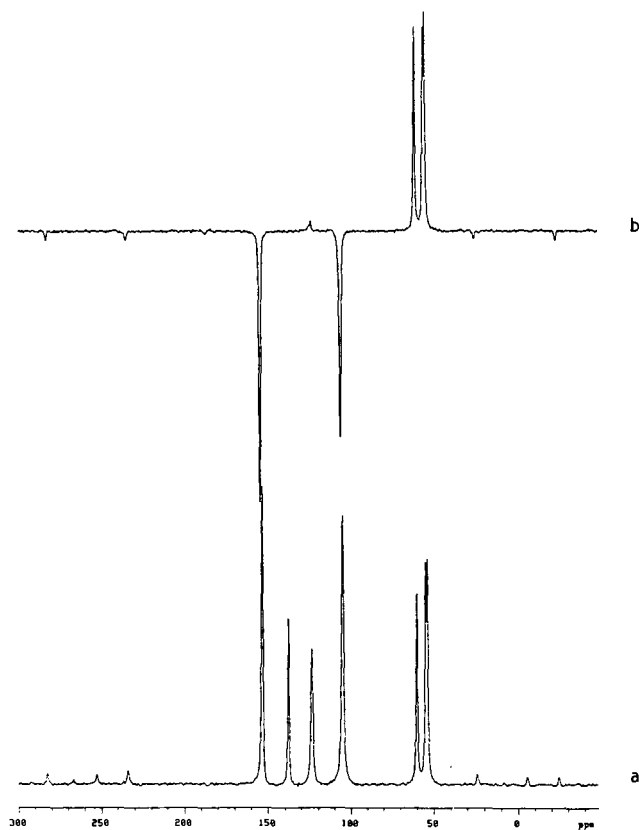
Figure 3. ^{13}C CP/MAS spectra of 1,2,3-Trimethoxybenzene (TMB) obtained with sample spinning rate of 6.0 KHz, contact time of 4 ms: a) the normal ^{13}C CP/MAS spectrum; b) spectrum obtained using the sequence in Figure 1a. The inner two aromatic resonances were saturated using the dephased DANTE sequence with offset frequencies centered at $to_1=124$ ppm and $to_2=138$ ppm and the outer two aromatic resonances were inverted using two 180° DANTE sequences with offset at $to_3=154$ ppm and $to_4=104$ ppm. Each dephased DANTE contains three 90°-DANTE of 20 pulses with pulse width 0.25 μs and a dephasing time between the sub-DANTE sequences of 16 ms.
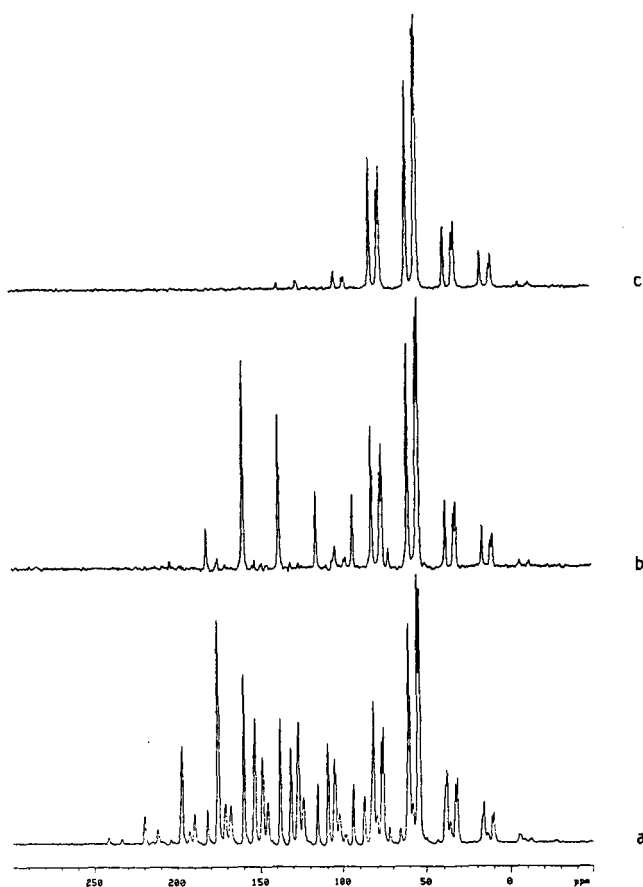
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Figure 4. Spectra of TMB obtained with sample spinning rate 1106±5 Hz and contact time of 4 ms: a) normal ^{13}C CP/MAS spectrum; b) spectrum obtained using three long DANTE sequences at transmitter frequency offsets of 126, 146 and 154 ppm in order to saturate these three spinning sideband families; c) spectrum obtained using four long DANTE sequences at 126, 146, 138, and 154 ppm to saturate the entire aromatic sideband family. The parameters for each long DANTE sequence are T_{pi}=0.25 μs, T_{di}=100 μs, N_i=150 and DD_i=8 ms.
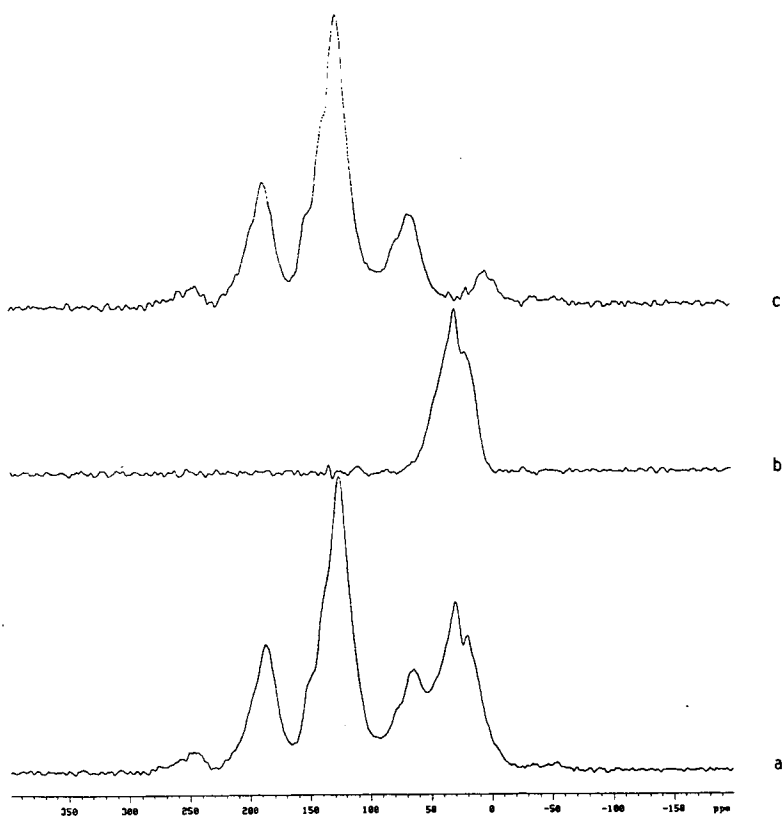
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Figure 5. ^{13}C CP/MAS spectrum of Lewiston Stockton coal obtained with a sample spinning rate 3000±30 Hz, and 1 ms contact time: a) the classical ^{13}C CP/MAS spectrum; b) application of four long DANTE sequences at 110, 126, 138 and 150 ppm to saturate the entire aromatic carbon spinning sideband family; c) subtraction of a from b. The parameters for each DANTE sequence are: T_{pi}=0.5 µs, T_{di}=30 µs, N_i=150, DD_i=2 ms;
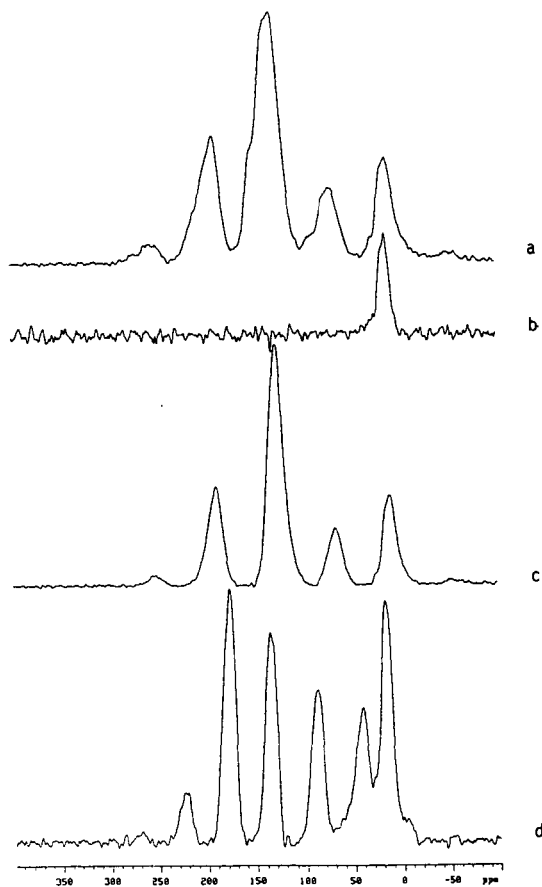
Figure 6.   Tailored excitation of the spinning sideband family for various types of carbons in Lewiston Stockton coal by combining the multiple offset DANTE method with the dipolar dephasing technique with a contact time of 1 ms, recycle delay time of 4s and sample spinning rate 3000 ± 30 Hz (6d with sample spinning rate 2100 ± 50 Hz), and $T_{pi}=0.5$ µs, $T_{di}=30$ µs, $N_i=150$, $DD_i=2$ ms; a) dipolar dephasing spectrum with dephasing time of 50 µs; b) spectrum obtained in a similar manner to Figure 5b except with a dephasing time of 50 µs inserted between the contact time and the first 90° pulse in the pulse sequence shown in Figure 1a; c) spectrum obtained in a similar manner to (b) except with three DANTE sequences at 138, 145 and 155 ppm used to saturate the phenolic and substituted aromatic sideband families; d) spectrum was again obtained in a similar manner to (b) but with four DANTE sequences used at 110, 120, 125 and 150 ppm to saturate the sideband families of the condensed and phenolic aromatic carbons. The remaining signals are due to methyl and substituted aromatic carbons.

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